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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: A METHOD OF PRODUCING MICROCELLULAR FOAMS AND MICROCELLULAR FOAMS OF SEMI-CRYSTALLINE POLYMERIC MATERIALS (57) Abstract A method for producing a microcellular foam from a semi-crystalline polymeric material. The material is heated to its melting point at an elevated pressure and then saturated with a uniform concentration of a gas. The pressure is then lowered causing bubble nucleation and growth within the material. The material is then quenched to prevent further foaming. Bubbles on the order of 5µm in diameter are produced with a bubble density of approximately 10 ¹⁰ bubbles/cm ³ .		

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A METHOD OF PRODUCING MICROCELLULAR
FOAMS AND MICROCELLULAR FOAMS
SEMI-CRYSTALLINE POLYMERIC MATERIALS

Background of the Invention

The ability to process polymers to desired
05 shapes and sizes is one of the properties that makes
polymers highly desirable for countless industrial
and commercial applications. As with all materials,
cost saving methods for processing and utilizing
polymers are of key importance. One method for
10 reducing the cost of a polymer article is through
the use of blowing agents which produce a foam,
thereby reducing the amount of polymer per unit
volume. Unfortunately, conventional foamed polymers
tend to exhibit a decrease in the mechanical prop-
15 erties.

Microcellular foams have been made in the past
by foaming amorphous polymeric materials such as
polystyrene. This process involves cell nucleation
at or near the glass transition temperature of the
20 polymer material and is more thoroughly described in
U.S. Patent 4,473,665 of Martini-Vvendensky, et al.
This patent, however, does not teach foaming of
semi-crystalline polymers such as polyethylene and
polypropylene.

25 Attempts to produce microcellular foamed
articles from semi-crystalline polymers using the
method employed for amorphous polymers have proven
to be failures. The three basic problems arising
when microcellularly foaming semi-crystalline

polymers result from the polymers' microstructure.
They are as follows:

- 1) low gas solubility in the crystalline domains,
- 05 2) the requirement to foam near the melting temperature rather than near the glass transition temperature, and
- 3) the physical size and structure of the crystals.

10 Taking the above characteristics of semi-crystalline polymers into account, it is apparent that conventional microcellular foaming techniques will fail to provide a desirable product when used on these polymer types.

15 Summary of the Invention

This invention pertains to closed cell microcellular foams of semi-crystalline polymeric materials and a method by which these microcellular foams are produced. More specifically, this invention per-
20 tains to a method for producing closed cell microcellular foams from semi-crystalline polymeric materials comprising the steps of:

- a) saturating the semi-crystalline polymeric material at an elevated pressure and at a
25 temperature at or above the melting temperature of the material with a uniform concentration of gas;
- b) shaping the polymeric material at an
30 elevated pressure to substantially prevent cell nucleation within the material;

- c) reducing the pressure to supersaturate the polymeric material with gas and thereby produce a microcellular structure in said material, and
- 05 d) lowering the temperature below the melting point of said polymeric material.

The products produced by this process have essentially an infinite number of uses. However, one major use is expected to be in the food service
10 industry. Polypropylene is used heavily in food container applications because it does not impart any flavor to the food contained within it, and because its thermal properties allow it to be filled with hot items. A microcellular foam of this material
15 would be ideal for food service applications due to its savings in raw materials (polypropylene), its insulating ability, its strength and its inertness to flavors.

Brief Description of the Drawings

20 The features and advantages of the invention will now be described with more detail in conjunction with the accompanying drawings. These drawings are not necessarily complete in every detail, but instead are intended to illustrate the
25 principles of the invention. For example, the dimensions and specific arrangement of various components of the apparatus may affect parameters of the process, such as the gas/polymer interface. Those skilled in the art will know, or be able to

ascertain using no more than routine experimentation, the optimum arrangement of apparatus for each application taking specific materials and operating conditions into account.

05 Figure 1 is a schematic representation of a horizontal extrusion die system used in producing microcellular foam from a semi-crystalline polymeric material.

10 Figure 2 is a schematic representation of a vertical extrusion die system used in producing a microcellular foam from a semi-crystalline polymeric material.

15 Figure 3 is a schematic representation of an injection molding apparatus used in producing a microcellular foam from a semi-crystalline polymeric material.

Detailed Description of the Invention

20 This invention relates to microcellular foams of semi-crystalline polymers and a method for producing these foams. In its most basic form, the invention involves heating a semi-crystalline polymer to a temperature at or above its melting point. A foaming gas is then supplied to diffuse into the molten polymer. Next, the polymer containing the diffused foaming gas is shaped, through
25 extrusion, injection molding or other forming processes. After being shaped, the polymeric body is subjected to a pressure reduction in the atmosphere surrounding it which triggers the foaming
30 process. Further cell growth is prevented by reducing the temperature to a point below the melting point of the polymeric material. This may

be done, for example, by quenching the material with water. Optionally, the pressure can be increased prior to or during the temperature reduction to assist in preventing further cell growth.

05 Microcellular foam is a polymeric foam with cell sizes smaller than about 100 micrometers (μm) and ideally in the range of about 5 to about 25 μm . These void diameters are found to be small enough to enhance or at least maintain the mechanical pro-
10 perties of the parent polymer.

 While often referred to as crystalline polymers, materials such as polypropylene and polyethylene exist in states which are either amorphous or semi-crystalline, depending upon the
15 process used to produce them. Ignoring the amorphous state, it is more accurate to term these materials semi-crystalline rather than crystalline since no material is entirely crystalline and free of amorphous domains. The crystalline domain of the
20 material is a region in which the molecules have a regular and ordered arrangement. This may be contrasted to the amorphous domains in which the structure is more random and disordered. Due to the absence of polymers with an absolute crystalline
25 structure, the term semi-crystalline is used here, as in the art, to denote polymeric materials containing crystalline domains.

 The glass transition temperature is distinguished from the melting temperature as follows.
30 Glasses are actually supercooled liquids of very high viscosity. The glass transition temperature is that temperature below which free rotations of the

polymer molecules cease because of intermolecular forces. In this state, the material is glassy. Above the glass transition temperature, the polymer is rubbery. All polymers have a glass transition
05 temperature. Semi-crystalline polymers also have a melting temperature above the glass transition temperature, above which the crystalline domains dissolve, leaving a fully amorphous material. Above
10 the melting point, these polymers are viscous or viscoelastic materials.

A schematic representation of a system for forming microcellular foams from crystalline polymers is shown in Figure 1. An extruder 30, is loaded with polymer pellets 1. These pellets are
15 heated to a temperature above their melting point and forced through the extrusion barrel 31 by a screw 32. The molten polymer 10 is forced by the extrusion screw 32 into a horizontal extrusion die 20. The die contains an aperture 22, through which
20 gas at a high pressure can be pumped to allow interaction between the polymer 10 and the gas at the polymer/gas interface 40. At this interface 40, gas will dissolve into the molten polymer. The polymer 10 then passes out of the die at exit 25, at
25 which point foaming begins due to the reduced pressure on the polymer shape. The material may then be quenched with cold water or other fluids to stop the foaming process. Optionally, the pressure can be increased prior to or during the reduction in
30 temperature to further assist in preventing further cell growth.

Figure 2 is a schematic representation of a system similar to that depicted in Figure 1; however

in Figure 2 the extrusion die 20' is in a vertical rather than a horizontal orientation. The advantage of this orientation lies at the polymer/die seal 100. This seal prevents the diffusion gas from
05 escaping from the die 20' through the die exit 25'. Gravitational force pulls the melted polymer 10' to the bottom of the die 20' thereby creating the seal 100 at a point anterior to the die exit 25'. This leads to a more uniform gas diffusion within the
10 melted polymer 10'. Otherwise, the operation of the system is similar to that depicted in Figure 1 and is described as follows.

An extruder 30', is loaded with polymer pellets 1'. These pellets are heated to a temperature above
15 their melting point and forced through the extrusion barrel 31' by a screw 32'. The molten polymer 10' is forced by the extrusion screw 32' into a vertically oriented extrusion die 20'. The die contains an aperture 22', through which gas at a high
20 pressure maybe pumped to allow interaction between the polymer 10' and the gas at the polymer gas interface 40'. At this interface 40', gas will dissolve into the molten polymer. Below this interface is the polymer/die seal 100 discussed
25 previously. The molten polymer 10' then passes out of the die at the die exit 25', at which point foaming begins due to the reduced pressure on the polymer shape. The material may then be quenched with cold water or other fluids or an increase in
30 pressure to stop the foaming process.

Figure 3 is a schematic representation of an injection molding system useful for producing

microcellular foams from crystalline polymers. The figure illustrates a number of known elements including an extruder 30'', extrusion barrel 31'', extrusion screw 32'', valve 44, nozzle 46, mold 48 and a clamping hydraulic pressure means 50. The pressure in the mold 48 is maintained above the foaming pressure of the gas at melt temperatures for the given initial saturation. When the temperature of the molded part is lowered to the appropriate nucleation temperature, the pressure is dropped and the part is allowed to foam. To keep the melt from nucleating prior to shaping, a pressure substantially equal to that within the extrusion barrel 31'' must be maintained within the mold cavity. The pressure can be supplied by a moveable wall 52 under hydraulic pressure for simple part geometries. When the nucleation temperature of the part is achieved the mold 48 is either expanded or cracked to allow the pressure to reach ambient pressure. The part will then expand as the polymer material foams to the final geometry. Many currently existing injection molding machines may be equipped with a moveable wall 52 to allow their use in this process.

Various gases can be used to supersaturate the polymeric material. For example, air, noble gases (such as argon), nitrogen or carbon dioxide can be used. The pressure of the gas on the raw material should be high enough to provide uniform saturation.

Semicrystalline polymers, such as polyethylene and polypropylene, are ideal candidates for foaming due to their low cost and good physical properties.

Satisfactory results have been obtained with gas saturation pressures between approximately 750 psig and 2500 psig for polypropylene. Saturation pressures below 750 psig have been found to result
05 in unevenly saturated samples, resulting in uneven nucleation and bubble growth.

When the material was saturated by nitrogen at a pressure of 1500 psig, the foamed material resulting therefrom was found to contain a bubble
10 density on the order of 10^{10} bubbles per cubic centimeter with each bubble of 5 microns in diameter.

Optionally, additives can be employed to enhance cell nucleation. For example, a material
15 such as sodium benzoate can be added to enhance cell nucleation.

Specific Examples

Foamed discs of semi-crystalline polymeric material were made by injection molding in the
20 following manner. A 2" diameter, 1/16" thick disc of the material to be foamed was placed in a pressure vessel and heated to a temperature above its melting point. For the materials employed herein, a temperature of approximately 173°C was
25 found to be satisfactory. The molten material was then saturated with 1500 psig of nitrogen for approximately 30 minutes. The temperature of the material was then lowered and the pressure was released shortly thereafter. The drop in both
30 temperature and pressure caused a spontaneous cell

or bubble nucleation and growth within the material and resulted in a foamed part approximately 1/8" thick.

The five following polymers were used with this method: Himont copolymer 7823 (polypropylene with 6.9% by weight ethylene), United States Steel copolymer (polypropylene with 6.9% ethylene), Shell nucleated polypropylene 5524, Shell polypropylene 5384, and Himont 101 polypropylene (with 40% talc by weight).

Microcellular foaming was most successful with the two copolymers. This is likely the effect of two copolymer characteristics: a) a smaller dropoff of the temperature-viscosity relationship near the melting point, and, b) the existence of internal interfaces at which bubbles can nucleate. The Shell nucleated polypropylene also foamed easily due to the large number of nucleation sites contained within the material. The other Shell polypropylene did foam but not as easily as the others because its interfacial energy is not high enough to provide energy for foaming. Finally, the talc-filled Himont was difficult to foam due to the very tight bonding between the talc particles and the polymer which interfered with foaming.

Equivalents

Those skilled in the art will recognize, or be able to ascertain, using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. For example, rather than allowing the foaming gas to

diffuse into the polymer melt in the die or injection mold, this can be done in the extrusion barrel during the extrusion process. Such equivalents are intended to be encompassed by the following claims.

CLAIMS

1. A method of producing a microcellular foam from a semi-crystalline polymeric material comprising:
 - 05 a) saturating the semi-crystalline polymeric material at an elevated pressure and at a temperature at or above the melting temperature of the material with a uniform concentration
10 of gas;
 - b) shaping the polymeric material at an elevated pressure to substantially prevent cell nucleation within the material;
 - 15 c) reducing the pressure to supersaturate the polymeric material with gas thereby causing nucleation and foaming and producing a microcellular structure in said polymeric material; and
 - 20 d) lowering the temperature below the melting point of said polymeric material.
2. The method of Claim 1 wherein the step of
25 saturating the material at an elevated pressure further comprises saturating the material at a pressure between approximately 750 psig and 2500 psig.
3. The method of Claim 1 wherein the microcellular
30 voids are on the order of about 1 to about 100 microns in diameter.

4. The method of Claim 1 wherein the microcellular voids are on the order of about 5 to about 25 microns in diameter.
- 05 5. The method of Claim 1 wherein the microcellular voids are approximately 10 microns in diameter.
- 10 6. The method of Claim 1 wherein the step of saturating the material at an elevated pressure with a uniform concentration of gas further comprises saturating the material with a uniform concentration of gas chosen from the group consisting of air, noble gases, nitrogen and carbon dioxide.
- 15 7. The method of Claim 1 wherein the step of reducing the temperature and pressure to a state where the material is supersaturated further comprises the steps of first reducing the temperature and then reducing the pressure.
- 20 8. The method of Claim 1 wherein the step of processing the material further comprises processing the material by die extrusion.
9. The method of Claim 1 wherein the step of processing the material further comprises processing the material by injection molding.
- 25 10. A closed cell, microcellular foam of a semi-crystalline polymeric material.

11. The material of Claim 10 wherein the polymeric material comprises a polymer of propylene.
12. The material of Claim 10 wherein the polymeric material comprises a polymer of ethylene.
- 05 13. The material of Claim 10 wherein the material contains microcellular voids on the order of about 1 to about 100 microns in diameter.
14. The material of Claim 10 wherein the material contains microcellular voids on the order of
10 about 5 to about 25 microns in diameter.
15. The material of Claim 10 wherein the microcellular voids are approximately 10 microns in diameter.

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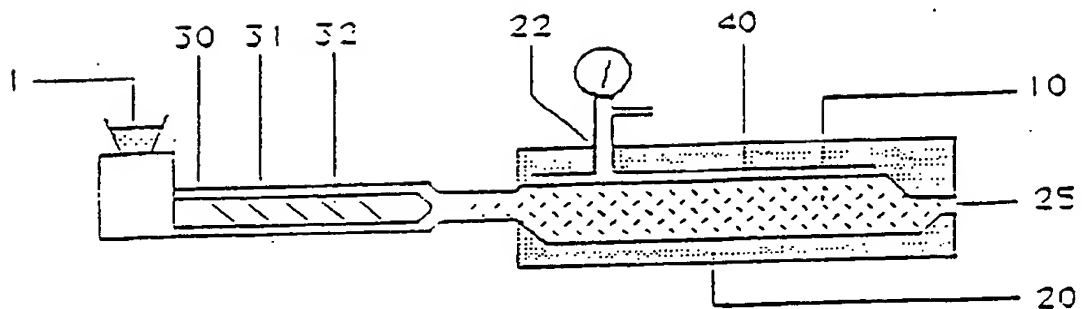


FIGURE 1

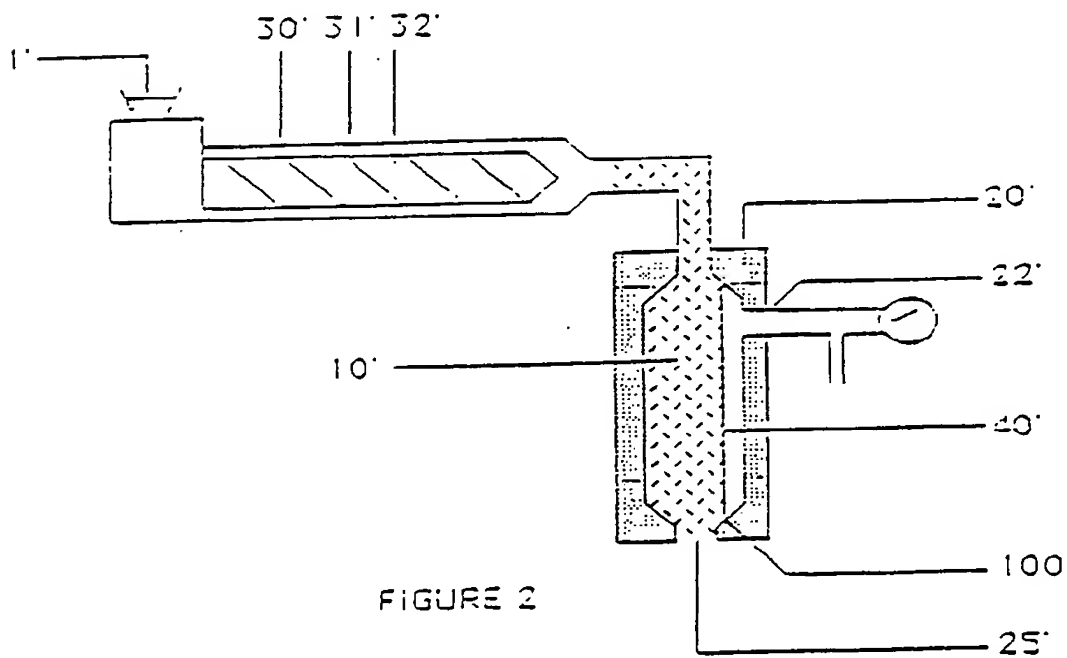


FIGURE 2

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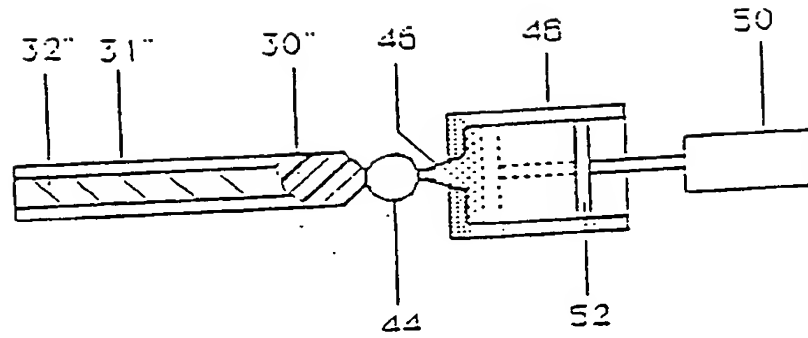


FIGURE 3



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(54) Title: A METHOD OF PRODUCING MICROCELLULAR FOAMS AND MICROCELLULAR FOAMS OF SEMI-CRYSTALLINE POLYMERIC MATERIALS (57) Abstract A method for producing a microcellular foam from a semi-crystalline polymeric material. The material is heated to its melting point at an elevated pressure and then saturated with a uniform concentration of a gas. The pressure is then lowered causing bubble nucleation and growth within the material. The material is then quenched to prevent further foaming. Bubbles on the order of 5µm in diameter are produced with a bubble density of approximately 10 ¹⁰ bubbles/cm ³ .		

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AMENDED CLAIMS

[received by the International Bureau on 28 March 1989 (28.03.89);
original claims 1,7-9 , 13-15 amended; other claims unchanged (3 pages)]

1. A method of producing a closed cell, microcellular foam from a semi-crystalline polymeric material, comprising the steps of:
 - a) saturating the semi-crystalline polymeric material at an elevated pressure and at a temperature at or above the melting temperature of the material with a uniform concentration of gas;
 - b) shaping the polymeric material at an elevated pressure to substantially prevent cell nucleation within the material;
 - c) reducing the pressure to supersaturate the polymeric material with gas thereby causing nucleation and foaming and producing a closed cell, microcellular structure in said polymeric material; and
 - d) lowering the temperature below the melting point of said polymeric material to prevent further cell growth.
2. The method of Claim 1 wherein the step of saturating the material at an elevated pressure further comprises saturating the material at a pressure between approximately 750 psig and 2500 psig.
3. The method of Claim 1 wherein the microcellular voids are on the order of about 1 to about 100 microns in diameter.

- 4 . The method of Claim 1 wherein the microcellular voids are on the order of about 5 to about 25 microns in diameter.
- 5 5. The method of Claim 1 wherein the microcellular voids are approximately 10 microns in diameter.
- 10 6. The method of Claim 1 wherein the step of saturating the material at an elevated pressure with a uniform concentration of gas further comprises saturating the material with a uniform concentration of gas chosen from the group consisting of air, noble gases, nitrogen and carbon dioxide.
- 15 7. The method of Claim 1 wherein the steps of reducing the pressure to a state where the material is supersaturated and lowering the temperature, further comprises the steps of first lowering the temperature and then reducing the pressure.
- 20 8. The method of Claim 1 wherein the step of shaping the material further comprises shaping the material by die extrusion.
9. The method of Claim 1 wherein the step of shaping the material further comprises shaping the material by injection molding.
- 25 10. A closed cell, microcellular foam of a semi-crystalline polymeric material.

11. The material of Claim 10 wherein the polymeric material comprises a polymer of propylene.
12. The material of Claim 10 wherein the polymeric material comprises a polymer of ethylene.
- 5 13. The microcellular foam of Claim 10 containing microcellular voids on the order of about 1 to about 100 microns in diameter.
- 10 14. The microcellular foam of Claim 10 containing microcellular voids on the order of about 5 to about 25 microns in diameter.
15. The microcellular foam of Claim 10 wherein the microcellular voids are approximately 10 microns in diameter.

STATEMENT UNDER ARTICLE 19

Claim Amendments

Claims 1, 7-9 and 13-15 have been amended.

In accordance with PCT practice, replacement pages to effect these amendments are attached.

Claim 1 differs from Claim 1 as filed in that the microcellular foam is more clearly defined as a closed cell microcellular foam. In step (d), the function of lowering the temperature to prevent further cell growth has been added.

Claim 7 differs from Claim 7 as filed to provide proper antecedent basis and to more clearly define the claim.

Claim 8 differs from Claim 8 as filed in that the two appearances of the word "processing" have been changed to "shaping".

Claim 9 differs from Claim 9 as filed in that the two appearances of the word "processing" have been changed to "shaping".

Claim 13 differs from Claim 13 as filed in that the word "material" has been changed to "microcellular foam". The form of the claim has also been changed.

Claim 14 differs from Claim 14 as filed in that the word "material" has been changed to "microcellular foam". The form of the claim has also been changed.

Claim 15 differs from Claim 15 as filed in that the word "material" has been changed to "microcellular foam".